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**APPLICATION FOR LETTERS PATENT**

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Homogenous Solid Solution Alloys For Sputter-  
Deposited Thin Films

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## HOMOGENOUS SOLID SOLUTION ALLOYS FOR SPUTTER-DEPOSITED THIN FILMS

### RELATED PATENT DATA

**[0001]** This patent claims benefit of priority under 35 U.S.C. §119 to U.S. Provisional Patent Serial No. 60/417,367, which was filed October 8, 2002.

### TECHNICAL FIELD

**[0002]** The invention pertains to sputtering components, such as, for example, physical vapor deposition targets; and methods of making sputtering components. The invention also pertains to sputter-deposited thin films.

### BACKGROUND OF THE INVENTION

**[0003]** Physical vapor deposition methodologies are frequently utilized for forming thin films of material. A diagrammatic view of a portion of an exemplary physical vapor deposition apparatus 10 is shown in Fig. 1. Apparatus 10 comprises a backing plate 12 having a sputtering target 14 bonded thereto. A semiconductive material wafer 16 is within apparatus 10 and provided to be spaced from target 14. A surface 15 of target 14 is a sputtering surface. In operation, sputtered material 18 is displaced from surface 15 of target 14 and utilized to form a coating (or thin film) 17 over wafer 16.

**[0004]** The backing plate/target assembly of Fig. 1 is shown in cross-sectional side view and top view, respectively, in Figs. 2 and 3. Backing plate 12 and target 14 join at an interface. The interface can comprise, for example, a diffusion bond between the backing plate and target, or a solder bond.

**[0005]** The backing plate/target assembly of Figs. 1-3 is an exemplary configuration, and it is to be understood that the invention described below can be utilized in other target assemblies besides that of Figs. 1-3. For instance, the invention can be utilized in monolithic target assemblies (where monolithic is used to refer to a target that is machined or fabricated from a single piece of material and is without combination with a backing plate). It also to be understood that sputtering can occur from surfaces of other components, besides a target (such as, for example, coils), during physical vapor deposition. For purposes of interpreting this disclosure and the claims that follow, the term "sputtering component" refers to any component from which material is sputtered during a physical vapor deposition process.

**[0006]** Metals are commonly utilized as sputtering target materials during fabrication of electronic devices, such as, for example, during fabrication of integrated circuitry associated with semiconductor structures. The metals can, in particular applications, be in the form of alloys. The metals are utilized, for example, in forming contacts and interconnections in microelectronic devices, as well as for forming anti-reflective coatings, etch stop layers, barrier layers relative to copper diffusion, metal gate electrodes, etc.

**[0007]** There can be numerous advantages to utilizing alloys rather than pure elements during sputter deposition of metallic materials. For instance, an alloying element can reduce electromigration effects in deposited conductive films (with an exemplary alloy being Al-Cu<sub>x</sub>). Alloys can improve physical and mechanical strength of target materials (with an exemplary alloy being Ti-Zr<sub>x</sub>). Alloys can form passivation layers in microelectronic circuits (with an exemplary alloy being Cu-Al<sub>x</sub>). Alloys can reduce the magnetic effect of a target material

(with an exemplary alloy being Ni-V<sub>x</sub>). Alloys can enable a specific electrical property of a metal to be tailored for utilization as a gate electrode in a transistor device, such as, for example, gate electrodes in complementary metal on semiconductor (CMOS) devices. Additionally, alloys can be utilized to reduce arcing by keeping a grain size small. For purposes of the present description, subscripts used in indicating compositions (i.e. x, y, and z) are greater than zero but are otherwise not limited to particular values, unless specifically indicated.

**[0008]** General alloying techniques have provided some success in forming suitable sputtering target constructions. However, there can be formation of secondary phases or precipitates within the sputtering target materials which limit suitability of the materials for various applications, or which prohibit achieving a desired property with a sputtering target material. Additionally, dissimilar erosion rates between a major constituent target material and a secondary phase can produce sharp boundaries or protruding precipitates on a sputtering surface of the target, resulting in arcing and/or resulting in undesirable defects in a sputter-deposited film formed on a semiconductor wafer.

## SUMMARY OF THE INVENTION

**[0009]** The invention encompasses formation and utilization of single phase, solid solution alloys from elemental metals. The alloys can be utilized in sputtering targets and other sputtering components. In particular aspects, the alloyed elements can form a complete series of solid solutions across an entire range of compositions of the alloyed elements. In other applications, the alloyed elements can form a series of solid solutions across a wide range of various compositions of the elements, with a sputtering component or other structure

being formed of a suitable alloy composition so that a solid solution between the alloyed elements exists during formation and utilization of the structure. Preferably, the sputtering components formed in accordance with aspects of the present invention have only one phase, and accordingly there is no formation of secondary ordered structures, or other secondary phase structures within the components. The secondary ordered structures typically do not exist at any temperature between the solidus point and room temperature in sputtering components of the present invention. It can be particularly desired that precipitates be eliminated entirely from sputtering components of the present invention.

**[0010]** Single-phase alloys of the present invention can have improved characteristics relative to alloys comprising multiple phases. For instance, solution strengthening within solid solution alloys of the present invention can improve the mechanical strength of the alloys. Single-phase alloys of the present invention can enable a strong sputtering target to be formed which has a higher resistance to recovery and grain growth than would a sputtering targeting having secondary phases therein. Also, sputtering materials comprising single-phase alloys can have a continuous range of physical and mechanical properties achieved by grading of the ratio of constituent elements across the ranges which form solid solution compositions.

**[0011]** An exemplary application of such materials is to allow a range of work function for transistor gates in integrated circuit devices. The elimination of secondary phases on a target sputtering surface can alleviate, and in particular cases eliminate, random or premature arcing along the sputtering surface during a sputtering operation. The utilization of a single phase alloy within target

materials (or other sputtering components) of the present invention can also enable reduced diffusion properties in target materials (or other sputtering components), as well as reduced diffusion properties in thin films sputter-deposited from the target materials (or other sputtering components).

**[0012]** An exemplary sputtering component of the present invention consists of a single phase corresponding to a solid solution of two or more elements in elemental form. The elements are designated to be in elemental form to indicate that the elements are not included in compounds. For instance, if nickel is stated to be in elemental form, such indicates that the nickel is not in the form of a nickel compound (with exemplary nickel compounds including nickel silicide and nickel aluminide).

**[0013]** In one aspect, the invention encompasses a method of forming a single phase solid solution mixed-metal material. The solid solution can comprise a base element and one or more additional elements or can have two or more elements present at atomic equivalence. For purposes of interpreting this disclosure and the claims that follow, a material having a first element M which is a majority element within the material can be referred to as having a base element. In other words, an M-based material has M as the majority element. A "majority element" is defined as an element which is present in larger concentration than any other element of a material. A majority element can be a predominate element of a material, but can also be present as less than 50% of a material. For instance, a first element M can be a majority element of a material in which the element M is present to only 30%, provided that no other element is present in the material to a concentration of greater than or equal to 30%.

**[0014]** A first element M can also be present in a solid solution material in an amount atomically equivalent to or less than one or more additional elements Q. For purposes of the present description, Q can represent a single element in a binary composition, or in alternative compositions can be a combination of 2 or more elements within the solid solution. Accordingly MQ can be a binary alloy or can be a ternary or higher order alloy.

**[0015]** In an exemplary process of forming a solid solution mixed-metal ingot, such ingot can be formed by combining a mixture of a first metal halide (M-halide) and at least one other metal halide (Q-halide) with a reducing agent to produce a mixed-metal product. The mixed-metal product is then melted to form a molten mixed-metal (M-Q) material. The molten mixed-metal material is cooled into a mixed-metal ingot comprising a solid solution of M-Q. The ingot comprises titanium and at least one other metal. The ingot has a purity of M and the at least one other metal Q of at least 99.95%.

**[0016]** In another aspect, the invention encompasses a method of electrolytically forming a mixed-metal solid solution material. A mixture of a first element M and at least one other metal Q is electrically deposited as a mixed-metal (M-Q) product. The mixed-metal product is melted to form a molten mixed-metal material. The molten mixed-metal material can be cooled into a single phase solid solution mixed-metal ingot. The ingot comprises M and the at least one other metal Q. The ingot can have a purity of M and the at least one other metal Q of at least 99.95%.

**[0017]** In another aspect, the invention encompasses an iodide transfer method of forming a single phase solid solution mixed-metal material. A mixture comprising first element M is provided in a reaction apparatus with iodine gas

and a heated substrate. M is reacted with the iodine gas to form an iodide which is subsequently transferred to the heated substrate. Heat from the substrate is utilized to decompose the iodide and produce a mixed-metal product comprising M. The mixed-metal product can be melted to form a molten mixed-metal material which can then be cooled into a solid solution mixed-metal ingot.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0018]** Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

**[0019]** Fig. 1 is a diagrammatic view of a portion of a prior art physical vapor deposition apparatus.

**[0020]** Fig. 2 shows a diagrammatic, cross-sectional side view of the prior art target/backing plate construction of Fig. 1. The construction corresponds to an ENDURA™ configuration available from Honeywell International Inc..

**[0021]** Fig. 3 is a top view of the prior art target/backing plate construction of Figure 2.

**[0022]** Fig. 4 is a flow-chart diagram illustrating methodology encompassed by the present invention.

**[0023]** Fig. 5 is a flow-chart diagram illustrating an exemplary reduction process of the present invention.

**[0024]** Fig. 6 is a diagrammatic, cross-sectional view of an apparatus utilized in an electrolytic process of the present invention.

**[0025]** Fig. 7 is a diagrammatic, cross-sectional view of an iodide process encompassed by the present invention.



**[0026]** Fig. 8 is a block diagram of a melting and ingot-forming process encompassed by the present invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0027]** This disclosure of the invention is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

**[0028]** The invention includes sputtering components (for example, sputtering targets) comprising, consisting essentially of, or consisting of a solid solution of two or more elements in elemental form. In particular aspects, the elements utilized in the sputtering components can all belong to the same group of the periodic table. However, it is to be understood that the invention also encompasses aspects in which at least some of the elements are chosen from different groups of the periodic table relative to one another. All numeric element group labels used in the present description indicate the numeric system (1-18) under the current convention of the International Union of Pure and Applied Chemistry (IUPAC).

**[0029]** It can be advantageous for a sputtering component to consist substantially or entirely of a single phase for at least the reason that such can: (1) lead to improved mechanical strength of the component; (2) alleviate, and even eliminate, premature arcing during sputtering from a surface of the component; and (3) reduce diffusion-related problems within the component, and within thin films sputter-deposited from the component.

**[0030]** In particular aspects, a sputtering component will have a surface (such as the surface 15 of sputtering target 14 in Fig. 1) of which at least 99 atomic % consists of a single phase. The single phase will correspond to a solid

solution of two or more elements in elemental form. In further aspects, at least 99.9% of the sputtering surface will consist of the single phase; and it can be preferred that an entirety of the sputtering surface consists of the single phase. Typically, a sputtering component will have a single composition throughout an entire volume of the component, and accordingly the entire volume of the sputtering component can be 99 atomic % of the single phase, in particular aspects 99.9% of the single phase, and in further aspects the entire volume of the sputtering component can consist of the single phase. Alternatively considered, a sputtering component (such as the target 14 of Fig. 1) can be considered to have a total mass, with such mass being understood to be the entirety of the sputtering component. It can be desired that at least 99 atomic % of the total mass consists of the above-described single phase, in further aspects it can be desired that at least 99.9% of the total mass consists of the single phase, and in yet further aspects it can be desired that the total mass consist only of the single phase.

**[0031]** It should be understood that in applications in which less than 100% of a sputtering component consists of a single phase, such can be due to incorporation of minor amounts of secondary materials within the target. Such secondary materials can be provided in low part per million concentrations to improve particular properties of a target, or of a film sputter-deposited from the target. For instance, low concentrations of materials can be incorporated into physical vapor deposition targets as dopants which are ultimately desired for adjusting various physical properties of a sputter-deposited thin film (with exemplary physical properties including barrier properties of the film relative to diffusion of particular materials, and electrical properties of the film).

**[0032]** The elements incorporated into the single phase of the sputtering component can be metallic elements and can, for example, be selected from group 1 of the periodic table, and in particular aspects can be selected only from group 1 of the periodic table. For instance, the elements can consist of Cs and Rb.

**[0033]** In other aspects, the elements utilized in the single phase of the sputtering component can include at least two elements selected from group 11 of the periodic table, and in specific aspects the elements can be selected only from group 11 of the periodic table. For instance, the elements M and Q can consist of Ag and Cu.

**[0034]** The single phase utilized in the sputtering component can alternatively include two or more elements selected from group 4 of the periodic table, and in particular aspects can include only elements selected from group 4. For instance, the sputtering component can include Zr and Hf. It is noted that titanium can be excluded from particular sputtering components of the present invention. It is also noted that titanium can be included in some sputtering components, alloys and films; particularly if the composition of the components, alloys or films includes three or more elements.

**[0035]** The two or more elements M and Q utilized in the single phase of the sputtering component can include at least two elements selected from group 5 of the periodic table, and in particular aspects the elements can be selected only from group 5 of the periodic table. For instance, the elements M and Q can be selected from the group consisting of Ta, Nb and V.

**[0036]** The two or more elements utilized in the single phase of the sputtering component can include at least two elements selected from group 6 of

the periodic table, and in specific aspects the elements can be selected only from group 6 of the periodic table. Accordingly, elements M and Q can be selected from the group consisting of Cr, Mo and W.

**[0037]** In yet further aspects, the two or more elements incorporated into the single phase of the sputtering component can include at least two elements selected from a combination of groups 8, 9 and 10 of the periodic table, and in specific aspects the two or more elements can be selected only from groups 8, 9 and 10 of the periodic table (it is noted that groups 8, 9 and 10 correspond to single group VIIB under the former IUPAC convention). Accordingly, the solid solution utilized in the sputtered component can, for example, be selected from the group consisting of Fe/Os, Fe/Ru, Co/Ir, Co/Rh, Ir/Rh, Ni/Pd, Ni/Pt, Co/Ni and Pd/Pt (with the solutions being described in terms of the constituents of the of solutions, and where no particular stoichiometry is indicated by the method of listing of the constituents). The described solutions are, of course, only a small subset of the total number of solutions that can be formed from two or more elements from groups 8, 9 and 10. Even though each of the solutions described only comprises two elements, it is to be understood that solid solutions utilized in sputtering components can also comprise 3 or more elements.

**[0038]** As mentioned above, sputtering components of the present invention can comprise mixtures of elements from different groups of the periodic table. For instance, the single phase solution utilized in sputtering components of the present invention can consist of Cu/Ni, Ta/Mo, Ta/W or Cr/Fe.

**[0039]** Some of the compositions listed above have solid phases throughout all possible ranges of the described mixtures of elements M and Q, whereas other compositions have solid phases throughout only some possible

ranges of mixtures of M and Q. For instance, only a partial range of the phase diagram of Co/Ni compositions is a single phase, similarly only a partial range of the phase diagrams of Ni/Pd, Ni/Pt, Cu/Ni, and Cr/Fe are solid solutions. Preferably, for purposes of the present invention, the relative concentrations of elements utilized in a sputtering component is chosen such that the elements form a single phase solid solution within the component during formation of the component, and such that the single phase is maintained during operation of the component. It can be desired that the single phase also be present in thin films sputter-deposited from the component.

**[0040]** In an exemplary aspect, the invention includes a sputtering component comprising a sputtering surface. At least 99 atomic% of the sputtering surface consists of a single phase corresponding to a solid solution of two or more elements in elemental form. The solid solution contains a first element M and one or more additional element Q. In particular instances M and at least one element comprised by Q are selected from the same group of elements or from combined groups 8, 9 and 10. Where Q is 2 or more elements, all elements comprised by Q can be from the same group or combined groups 8, 9 and 10. Alternatively Q can comprise elements from differing groups.

**[0041]** In some instances, at least 99.9 atomic% of the sputtering surface can consist of the single phase, and in some aspects an entirety of the sputtering surface consists of the single phase.

**[0042]** The sputtering component can be in the form of a physical vapor deposition target. The physical vapor deposition target can have a total volume, and at least 99 atomic% of the total volume can consist of the single phase, at

least 99.9 atomic% of the total volume can consist of the single phase, or an entirety of the total volume can consist of the single phase.

**[0043]** The invention includes a thin film sputter-deposited from the single phase solid solution sputtering component. The deposited film can also comprise single phase solid solution and can, in some instances, contain the same percentage of solid solution material as did the originating component.

**[0044]** The two or more elements of the sputtering component can include at least two elements selected from group 1 of the periodic table, and can include only elements selected from group 1 of the periodic table. The two or more elements can, for example, consist of Cs and Rb. The invention can include a thin film sputter-deposited from the sputtering component which includes at least two elements selected from group 1 of the periodic table.

**[0045]** The two or more elements of the sputtering component can include at least two elements selected from group 11 of the periodic table, and can include only elements selected from group 11 of the periodic table. The two or more elements can, for example, consist of Ag and Cu. The invention can include a thin film sputter-deposited from the sputtering component which includes at least two elements selected from group 11 of the periodic table.

**[0046]** The two or more elements of the sputtering component can include at least two elements selected from group 4 of the periodic table, and can include only elements selected from group 4 of the periodic table. The two or more elements can, for example, consist of Zr and Hf. The invention can include a thin film sputter-deposited from the sputtering component which includes at least two elements selected from group 4 of the periodic table.

**[0047]** The two or more elements of the sputtering component can include at least two elements selected from group 5 of the periodic table, and can include only elements selected from group 5 of the periodic table. The two or more elements can be, for example, selected from the group consisting of Ta, Nb, and V. The invention can include a thin film sputter-deposited from the sputtering component which includes at least two elements selected from group 5 of the periodic table.

**[0048]** The two or more elements of the sputtering component can include at least two elements selected from group 6 of the periodic table, and can include only elements selected from group 6 of the periodic table. The invention can include a thin film sputter-deposited from the sputtering component which includes at least two elements selected from group 6 of the periodic table.

**[0049]** The two or more elements of the sputtering component can include at least two elements selected from groups 8, 9 and 10 of the periodic table, and can include only elements selected from groups 8, 9 and 10 of the periodic table. The solid solution of the sputtering component can be, for example, selected from the group consisting of Fe/Os, Fe/Ru, Co/Ir, Co/Rh, Ir/Rh, Ni/Pd, Ni/Pt, Co/Ni and Pd/Pt. The invention can include a thin film sputter-deposited from the sputtering component which includes at least two elements selected from groups 8, 9 and 10 of the periodic table.

**[0050]** As further examples, the sputtering component can comprise, consist essentially of, or consist of a solid solution selected from the group consisting of Cu/Ni, Ta/Mo, Ta/W and Cr/Fe. Thin films can be formed from these targets to comprise, consist essentially of, or consist of Cu/Ni, Ta/Mo, Ta/W or Cr/Fe.

**[0051]** The invention includes methods for forming mixed-metal materials, and in particular applications encompasses new methods of forming ingots comprising the solid solution mixtures of metals described above. In particular embodiments, a mixed-metal feedstock comprising M and Q is produced by one or more of a reduction process, electrolysis process or iodide process, and such feedstock is subsequently melted to form a homogeneous molten mixture of the metals. The molten mixture is then cooled to form a mixed-metal ingot comprising a solid solution of M and Q. The ingot can be subsequently utilized to form materials in which solid solution mixed-metal compositions are desired. For instance, the ingot can be utilized in forming sputtering targets. It is noted that various reduction processes, electrolysis processes and iodide processes have been described previously in U.S. Patent Nos. 6,063,254, and 6,024,847; and in U.S. Patent Application Serial No. 08/994,733. U.S. Patent Nos. 6,063,254, and 6,024,847, and U.S. Patent Application Serial No. 08/994,733 are all incorporated herein by reference.

**[0052]** In particular applications, the mixed-metals provided within the ingot will be M-based materials (i.e. first-element M will be the majority element within the mixed-metal), and in other applications the mixed-metals will not comprise a majority of a single element. The metal mixtures can be any of the binary or higher order compositions described above, preferably with element ratios within ranges appropriate for solid solution formation. Either M-based mixtures or mixtures comprising 2 or more elements in atomic equivalence can ultimately be utilized in forming sputtering targets.

**[0053]** An exemplary use for solid solution sputtering targets of the invention can be for sputter-deposition of a film on a semiconductor substrate. In



particular instances, the deposited film will comprise a solid solution, and can consist essentially of a solid solution or consist of a solid solution. Films can be utilized as a barrier layer to impede migration of a metal from a metal-containing component to other components associated with the semiconductor substrate. Specifically, the film can be provided between a metal-containing component and other components of a semiconductor substrate, and can be utilized to prevent metal migration from the metal-containing component to the other component associated with the substrate.

**[0054]** To aid in interpretation of the claims that follow, the terms “semiconductive substrate” and “semiconductor substrate” are defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term “substrate” refers to any supporting structure, including, but not limited to, the semiconductive structures described above. An exemplary semiconductive material is silicon, such as, for example, monocrystalline silicon.

**[0055]** Among the barrier layers that can be particularly useful are layers comprising, consisting essentially of, or consisting of  $Ti_xHf_yN_z$ , or  $Ta_xV_yN_z$ , for example, and such layers can be formed from sputtering targets comprising, consisting essentially of, or consisting of  $Ti_xHf_y$ , and/or  $Ta_xV_y$  (where x, y and z are not limited to any particular values).

**[0056]** Additional useful layers or films that can be formed from single phase solid solution targets of the invention include, for example, barrier layers of  $Zr_xHf_yN_z$  and/or  $Ta_xMo_yN_z$  (where x, y and z are not limited to any particular

values, and each is greater than zero). Such layers can be formed from sputtering targets comprising, consisting essentially of, or consisting of  $Zr_xHf_y$  or  $Ta_xMo_y$ . Single phase solid solution targets of the invention comprising the compositions disclosed above can also be used to form conductive layers and insulating protective layers (such as nitride layers). Gate materials having a particular work function can be produced by varying the ratio of M to Q, (and/or a ratio of elements that are comprised by Q) in the single phase targets of the invention. This compositional element ratio adjustment technique can also be used to tailor targets to produce desired physical, mechanical and/or thermal properties including resistivity, mechanical strength and thermal expansion coefficient of deposited films or layers.

**[0057]** A method encompassed by the present invention is shown in the flow chart of Fig. 4. At an initial step 20, a mixture of metallic elements is provided. The mixture will typically comprise a first metal M and one or more additional elements Q, and in particular embodiments can exclude both titanium and zirconium. The elements can be in an elemental form in the mixture of step 20, or can be provided as molecular components. For instance, M can be provided as, for example, elemental M or an M-halide (i.e.  $MCl_x$ ).

**[0058]** The mixture of step 20 is provided to one or more of a reduction process 22, an electrolysis process 24, or an iodide process 26. In the diagram of Fig. 4, the reduction process 22 is shown connected through a dashed arrow to electrolysis process 24, which in turn is shown connected through a dashed arrow to iodide process 26. The dashed arrows show that the processes 22, 24 and 26 can be optionally conducted sequentially relative to one another. For instance, a material from step 20 can be provided to reduction process 22, and

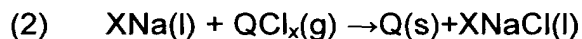
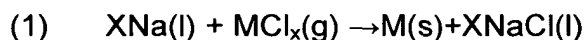
then subsequently provided from reduction process 22 to electrolysis process 24, and subsequently provided from electrolysis process 24 to iodide process 26.

**[0059]** Alternatively, the material from step 20 can be provided to reduction process 22, and then not submitted to either electrolysis process 24 or iodide process 26. Further, although the arrows between processes 22, 24 and 26 are shown proceeding in particular directions, it is to be understood that the processes connected by the dashed arrows can be connected in reverse to the shown methodology. For instance, material from electrolysis process 24 can be provided to reduction process 22, rather than the shown flow proceeding from reduction process 22 to electrolysis process 24. However, the shown flow can be a preferred flow orientation, in that the electrolysis process is generally considered to be a process for further purification of material after a reduction process, and the iodide process is considered to be a process which can lead to additional purification beyond that accomplished by either electrolysis process 24 or reduction process 22.

**[0060]** After the flow of material through one or more of processes 22, 24 and 26, the material is considered a product. The product is subjected to the processing of step 28, which comprises melting the product, and subsequently cooling the molten material to form an ingot. The ingot will have a mixture of elements contained therein, with such mixture reflecting at least some of the original mixture of metallic elements utilized in the composition of step 20. However, the final composition formed in the ingot of step 28 may have a different stoichiometric relationship of component elements than the mixture of step 20, as the kinetics and/or thermodynamics of processes 22, 24 and 26 may favor one metallic material relative to another.

**[0061]** The processes of steps 22, 24, 26 and 28 are described in more detail in Figs. 5-8. Referring initially to Fig. 5, the reduction process of step 22 is further illustrated. The shown process forms a mixed-metal material consisting essentially of, or consisting of, an MQ alloy. Initially,  $QCl_x$ ,  $MCl_x$ , and a reductant (for example, sodium or magnesium metal) are mixed. A resulting exothermic reaction produces an alloy of M and Q. The relative proportions of M and Q within the alloy are approximately proportional to the proportions of  $MCl_x$  and  $QCl_x$  utilized. Accordingly, an M-based binary alloy can be formed by utilizing a higher proportion of  $MCl_x$  relative to  $QCl_x$ , and an M-based alloy comprising more than two elements can be formed by utilizing a higher percentage of  $MCl_x$  relative to the chloride of any single element comprised by Q. Although the invention is described with reference to an embodiment utilizing metal chloride reactants, it is to be understood that other metal halides can be utilized in addition to, or alternatively to, the metal chlorides.

**[0062]** The reactants utilized in the reduction process of Fig. 5 will typically be in a gaseous or liquid form. For instance, the reductant can comprise molten sodium and the  $QCl_x$  and  $MCl_x$  can be in gaseous form. Accordingly, the reactions occurring in the reduction process can be summarized as reactions (1) and (2) below, in which s = solid phase; l = liquid phase and g = gas phase.



**[0063]** The M(s) and Q(s) can form a mixed-metal sponge. Such sponge can be subsequently melted and cooled to form an ingot, or can be utilized as a

feedstock in either the electrolytic process 24 of Fig. 4 or the iodide process 26 of Fig. 4.

**[0064]** If the formed alloy is an M-based alloy, then the total Q metal content of a material produced by the process of Fig. 4 can be any value so long as no single element comprised by Q equals or exceeds the content of M. In particular aspects, the content of Q in a range of from 0.001% to 50%, such as, for example, a range of from 0.001% to 10%. In particular embodiments, the total Q metal content of the material will be at least 0.01%, in further embodiments will be at least 0.1%, in yet other embodiments will be at least 1%, and in yet other embodiments will be at least 2%. The amount of Q in the mixed-metal material will be provided to a sufficient concentration in the material that Q is present at greater than 5 ppm in a material pure to 5N5, greater than 50 ppm in a material pure to 4N5, greater than 500 ppm in a material pure to 3N5, or greater than one part per thousand in a material pure to 3N.

**[0065]** If the mixed-metal material is subsequently melted and utilized to form an ingot as shown in step 28 of the Fig. 4 process, and if such melting occurs without intervening processes occurring between the reduction process and the melting process, the relative proportion of Q in a formed ingot will be the same as that of the mixed-metal product formed by the reduction process of Fig. 5.

**[0066]** If the formed alloy is not an M-based alloy, then at least one of the additional elements comprised by Q will be atomically equivalent to M. Additional elements comprised by Q can be present in the alloy at amounts atomically less than or equal to M.

**[0067]** In particular embodiments, the reduction process of Fig. 5 can be utilized to form an alloy consisting of M and Q, as shown. In such processes, the material can be M-based, with the only other metal besides M being those comprised by Q.

**[0068]** Referring next to Fig. 6, the electrolysis process 24 of Fig. 4 is described in more detail. Specifically, Fig. 6 illustrates an apparatus 50 which can be utilized for an electrolytic procedure of the present invention. Apparatus 50 comprises a furnace 52. An anode 54 and cathode 56 are provided within furnace 52. A metal feedstock 58 is provided against anode 54. Metal feedstock 58 can comprise M and one or more additional metals Q. In particular embodiments, the metal feedstock can comprise two or more elements from a single group selected from groups 1, 4, 5, 6 or 11 of the periodic table. In alternate embodiments the metal feedstock can comprises two or more elements selected from combined groups 8, 9 and 10 of the periodic table. In other embodiments, the metal feedstock can comprises one or more elements selected from differing groups of the periodic table. Exemplary feedstocks comprising metals from differing groups include feedstocks comprising one of the following combinations: Cu/Ni, Ta/Mo, Ta/W or Cr/Fe.

**[0069]** An electrolyte 60 is provided between the anode and the cathode. The electrolyte can comprise a salt, such as, for example, sodium chloride or magnesium chloride, and can be in a molten form due to a temperature maintained by furnace 52.

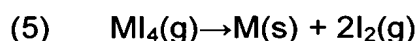
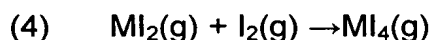
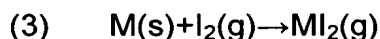
**[0070]** In operation, an electrical voltage is provided between anode 54 and cathode 56, and metal is electrolytically transferred from mixture 58 to cathode 56 to form a mixed-metal product 62 at cathode 56. Although mixture

58 is described as being provided against an anode 54, it is to be understood that anode 54 can be considered an electrical interconnection to mixture 58, and that mixture 58 can be considered to effectively be the "anode" during the electrolytic transfer reaction. The composition of mixed-metal product 62 can be determined, in part, by the voltage supplied to apparatus 50. Accordingly, apparatus 50 can be utilized for purification of a mixed-metal product relative to the material 58 provided at anode 54.

**[0071]** An aspect of the present invention is to form a mixed-metal product at cathode 56. For instance, if a majority element is M, then the material at cathode 56 will preferably comprise at least 0.001% of elements other than M. The amount and type of elements provided at cathode 56 can be determined by the voltage utilized for apparatus 50 and the starting material 58. Specifically, if a voltage window of  $\pm 0.7$  volts from the reduction potential for conversion of  $M^{2+}/M$  is utilized, a wider number of elements can be incorporated into product 62 than if a voltage window of  $\pm 0.5$  volts from the reduction potential for conversion of  $M^{2+}/M$  is utilized. Preferably, a voltage window will not exceed more than  $\pm 0.7$  volts from the reduction potential for a majority element to avoid adding excessive impurity to product 62.

**[0072]** Referring next to Fig. 7, an iodide process which can be utilized for step 26 of Fig. 4 is diagrammatically illustrated. Specifically, Fig. 7 shows an apparatus 100 comprising a reaction chamber 102. A feedstock 106 is provided within reaction chamber 102, and a heated substrate 104 extends into reaction chamber 102. Feedstock 106 comprises at least 2 different metals, and can, for example, comprise a majority metal M. An iodine gas 108 is provided within reaction chamber 102. In operation, iodine gas 108 transports metal from

feedstock 106 to heated substrate 104. The metal is then deposited onto substrate 104 to form a product 110. The transport of a metal from feedstock 106 to heated substrate 104 is described below with reference to reactions (3)-(5), and specifically is described with respect to formation of an exemplary metal.



**[0073]** Accordingly, the metal M is converted to an iodide, and the iodide is subsequently decomposed at the heated substrate 104 to deposit M-material 110. The reactions described above are merely exemplary reactions, and it is to be understood that the chemistry of metal transport in apparatus 100 can comprise other reactions in addition to, or alternatively to, those described.

**[0074]** A rate of transfer of a material from feedstock 106 to product 110 can depend on, among other things, a temperature differential between feedstock 106 and substrate 104, a concentration of iodine, and kinetics of reaction of a particular metal with iodine to form an iodide, as well as kinetics of reaction of a particular metal iodide to decompose to form the metallic element. Accordingly, if feedstock 106 comprises a mixture of elements, the product 110 can comprise a mixture having a different stoichiometry than that initially present as feedstock 106 due to, for example, differences in kinetics of iodide formation of various metallic iodides, and/or differences in kinetics of iodide decomposition of various metallic iodides.

**[0075]** Feedstock 106 can comprise two or more elements from a single group selected from groups 1, 4, 5, 6 or 11 of the periodic table. In alternate embodiments metal feedstock 106 can comprises two or more elements



selected from combined groups 8, 9 and 10 of the periodic table. In other embodiments, the metal feedstock can comprises one or more elements selected from differing groups of the periodic table. Exemplary feedstocks comprising metals from differing groups include feedstocks comprising one of the following combinations: Cu/Ni, Ta/Mo, Ta/W or Cr/Fe.

**[0076]** Also, product 110 can comprise two or more elements from a single group selected from groups 1, 4, 5, 6 or 11 of the periodic table. In alternate embodiments product 110 can comprises two or more elements selected from combined groups 8, 9 and 10 of the periodic table. In other embodiments, the metal product 110 can comprises one or more elements selected from differing groups of the periodic table. Exemplary products comprising metals from differing groups include products comprising one of the following combinations: Cu/Ni, Ta/Mo, Ta/W or Cr/Fe.

**[0077]** Fig. 8 is a block diagram description of a system which can be utilized for the processing of step 28 of Fig. 4. Specifically, Fig. 8 illustrates a system 150 comprising a feed port 154, a cooled hearth 156, and a mold 158. In operation, a feed material is poured through port 154 and melted by vacuum melting (such as, for example, with an electron beam gun) to form a homogeneous molten mixture of the elements present in the feed material. The molten mixture is subsequently poured into cooled hearth 156, and then flowed into a mold 158. Mold 158 can be in the form of, for example, an ingot can. Accordingly, the material flowed into mold 158 can cool to form an ingot. The ingot will preferably have a single phase solid solution composition of the elements initially present in the feed material.

**[0078]** The feed material provided to apparatus 150 can be a product of either the reduction process of step 22 of Fig. 4, the electrolysis process of step 24 of Fig. 4, or the iodide process of step 26 of Fig. 4. Regardless, the feedstock will preferably comprise a mixture of metals, such as, for example, an M-based material having at least 0.001% of non-M metals; or a composition having atomically equivalent amounts of M and at least one of the elements comprised by Q, (with no additional element being present in the composition at a greater atomic % than M). If the feed material is M-based, the content of other metals Q of the ingot can be any value so long as no single element comprised by Q is present at an amount equal to or exceeding the M content. In particular instances, the Q content of the ingot can be in a range of from 0.001% to 50%, such as, for example, a range of from 0.001% to 10%. The Q content can be, for example, at least 0.01%, and in particular embodiments can be at least 0.1%. Alternatively, if the material formed in the ingot is a non single-element based material, the at least one metal comprised by Q will be present in an amount equivalent to M, and any other elements comprised by Q will be present at an amount less than or equal to M.

**[0079]** A cooled ingot formed by the process of Fig. 8 can be utilized for forming a sputtering target. Sputtering targets comprising a solid solution of metallic elements can be useful in sputtering processes in which it is desired to form layers or films including but not limited to barrier layers, conductive layers, gate layers, and insulative protective layers. These targets can be particularly useful since they can be tailored to achieve a layer having a desired property including work function, resistivity, thermal expansion coefficient, mechanical strength, etc.

**[0080]** For sputtering applications of the present invention it can be desired that a target comprise a single phase solid solution throughout of all of the elements present in the sputtering target. Methodology of the present invention can enable such solid solution to be formed. Specifically, since methodology of the present invention melts a mixed-metal feedstock, methodology of the present invention can form a solid solution mixed-metal ingot which can in turn be utilized to form a sputtering target with a solid solution mixed-metal composition throughout.

**[0081]** There has not been a process developed in the prior art for forming a sputtering target consisting of a solid solution of the described compositions of one or more of the listed elements, but methodology of the present invention can enable such solid solution targets to be formed. In particular instances, the targets of the invention can have single phase solid solution throughout.

**[0082]** In compliance with the statute, the invention has been described in language more or less specific as to structural and methodical features. It is to be understood, however, that the invention is not limited to the specific features shown and described, since the means herein disclosed comprise preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.